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Anne Comblez, Anne-Laure Bussy, Jean-Marie Mouchel, Daniel R. Thévenot. LABORATORY SIMULATION FOR HEAVY METAL EVOLUTION IN CSO POLLUTED RIVER SEINE SEDIMENTS AND INTERSTITIAL WATERS. ICUSD, 1996, Hanover, Germany. hal-01180065

HAL Id: hal-01180065

<https://hal.science/hal-01180065>

Submitted on 24 Jul 2015

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LABORATORY SIMULATION FOR HEAVY METAL EVOLUTION IN CSO POLLUTED RIVER SEINE SEDIMENTS AND INTERSTITIAL WATERS

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KEYWORDS : Combined sewer overflow, river sediment, diagenesis, heavy metals.

INTRODUCTION

The River Seine is a very small stream, compared to the important population and the numerous activities of the district of Paris which have grown within its basin. It is now strongly constrained by anthropogenic influences such as dams, reservoirs, or sewage work outlets. Yet, a notable part of the wastes, produced within the basin is directly discharged into the river.

In order to assess the impact of such urban discharges on the river ecosystem, sediment cores and interstitial waters have been collected downstream and upstream Paris (Estèbe *et al.*, 1993, 1994; Bussy *et al.*, 1994). The results of these campaigns have shown a heavy metal contamination of suspended solids (SS) through Paris, and have demonstrated that storm sewer overflows are a major source of trace metals. However, spatial and temporal sediment heterogeneities as well as SS deposition and resuspension phenomenon hamper a good approach of the processes involved in heavy metal evolution during sediment diagenesis (Bussy & Estèbe, 1993). To avoid these problems, it has been attempted to simulate, in a laboratory experiment, the River Seine water-sediment interface. This paper describes the river Seine sediment diagenesis reactions, and the corresponding dissolved species fluxes, after receiving solids from a combined storm sewer overflow (CSO). Two successive experiments have been performed, using two different solid ratios.

EXPERIMENTAL

Pilot

The pilot is mainly composed by a ten litre Nylon reactor, filled with the experimental medium, and placed under a nitrogen atmosphere (figure 1). The reactor content is composed by a particulate phase, covered with a partly circulating aqueous phase,

simulating the river flow. This water is aerated by bubbling with cleaned air.

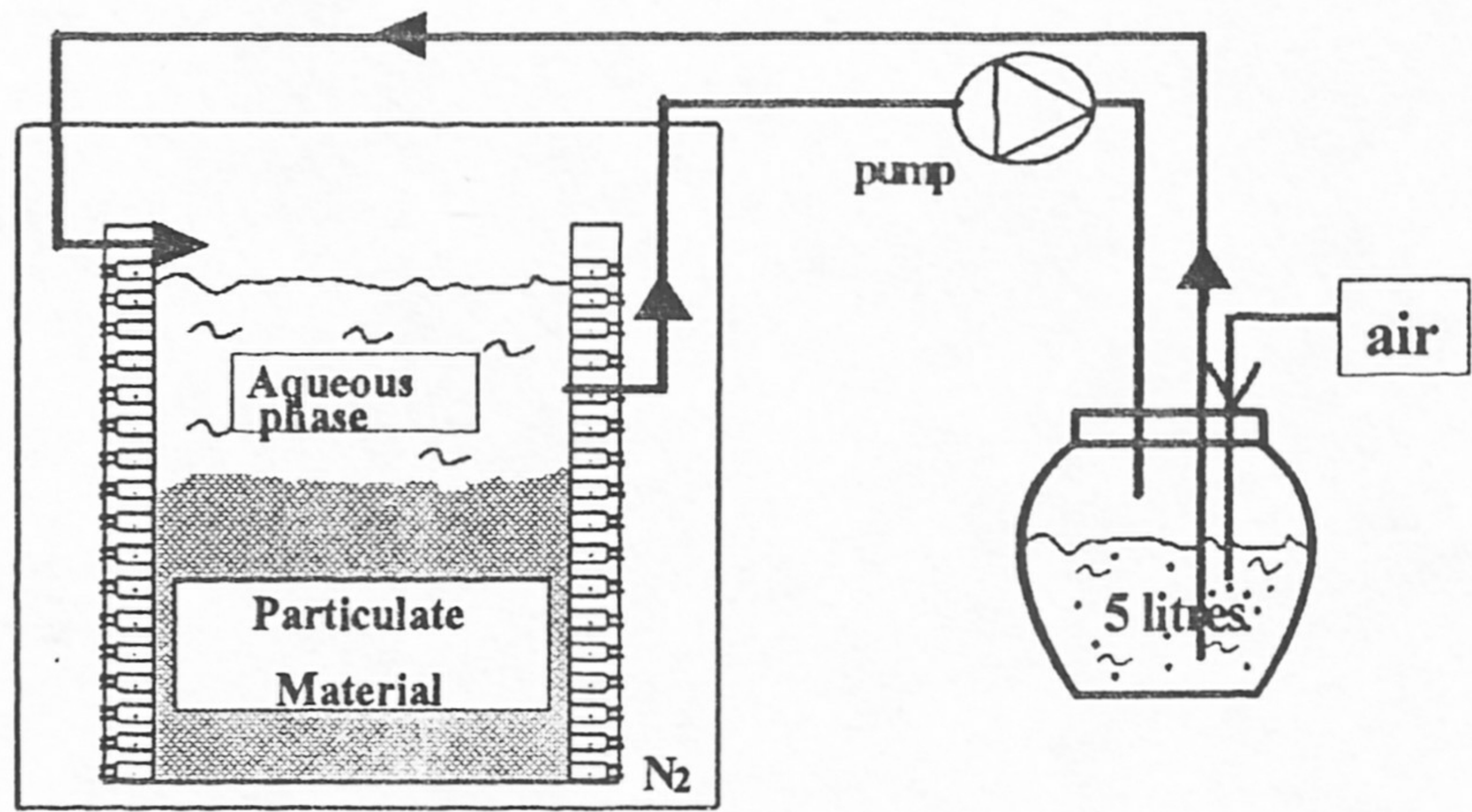


Figure 1: Pilot general view

The sampling technique used for this study is based on the dialysis of interstitial water through the reactor faces. Each wall is designed as a peeper. It contains 18 cells, filled up with 9 ml of deionized water (Millipore, MilliQplus 185), and separated from the experimental medium by a Nylon dialysis membrane (0.2 μm porosity, PALL, Biotec A). Small channels link each cell to the reactor wall outer face. They allow the sampling of the cell water, once equilibrated with the sediment interstitial water. The filling of the cells with fresh deionized water is performed by the same channels, after the sample collection. All the material was, at least, acid cleaned and rinsed with deionized water.

Particulate and aqueous material

Polluted SS were collected during storm CSO's into the river Seine, downstream Paris. After a 24 hour settling and a 2,600 g centrifugation, the wet sample was mixed with river Seine sediments collected upstream Paris, using a sampler described by Estèbe *et al.* (1995). Some river water was also sampled the same day, at the upstream site, in an acid washed polyethylene bottle. Table 1 gives sampling dates and mixing ratios for both experiments. Both particulate phases were mixed together under room atmosphere and placed inside the reactor. The resulting sediment was thus, at least partially oxygenated at the beginning of the experiment. River water was added at the top of the resulting 20 cm sediment column. The pilot was left to evolve during three months, at room temperature (25-30°C).

Table 1 : Sampling dates and mixture ratios (dw/dw) of experimental solid phases

	Sample source	Collection date	Mixture ratio: SS/sediment
1 st experiment	CSO SS at Clichy	28/07/94	1:2
	Seine sediment at Vitry	05/08/94	
2 nd experiment	CSO SS at Clichy	24/04/95	1.5
	Seine sediment at Vitry	05/05/95	

Water sampling

The first experience gave 7 series of pore water samples which were collected after a 1 month period of particulate phase stabilisation. The 8 series of samples from the second study have been collected between the 1st and the 16th weeks. Each time, the emptied cells were filled up with new deionized water, for the next collection. Resulting water samples were divided into 3 fractions. Nitric acid (0.01 mol/l, Merck, Suprapur) was added to the first one, in order to preserve it from metal adsorption on container walls before AAS analysis (Struempfer, 1973). Dissolved sulphides were stored by precipitation with 3 mmol/l zinc acetate, at a basic pH. The last fraction was frozen before the main dissolved species analysis.

Analyses

Dissolved copper, zinc and cadmium were analysed by graphite furnace AAS (Perkin-Elmer, 1100B and HGA 700). Dissolved iron and particulate metals were analysed using the same equipment, set up for flame technique. Flameless AAS results were verified with an US artificial river water certified standard (NIST, SRM 1643c). Dissolved sulphides were analysed by colorimetry, using the method described by Cline (1969). Dissolved ammonium ions were also measured using a spectrophotometric technique, modified from the indophenol procedure taken from AFNOR NF T 90-015 (Mouchel *et al.*, 1992). Sulphates and nitrates were analysed by ionic chromatography (Dionex, QIC), using a carbonate/bicarbonate buffer (1.8 and 1.7 mmol/l) as carrier fluid. Dissolved organic carbon and dissolved carbonates were analysed by a total organic carbon analyser (Astro 2001, system II).

RESULTS AND DISCUSSION

Sediment microbial activity

The 2 experiments gave similar results for non metallic dissolved species.

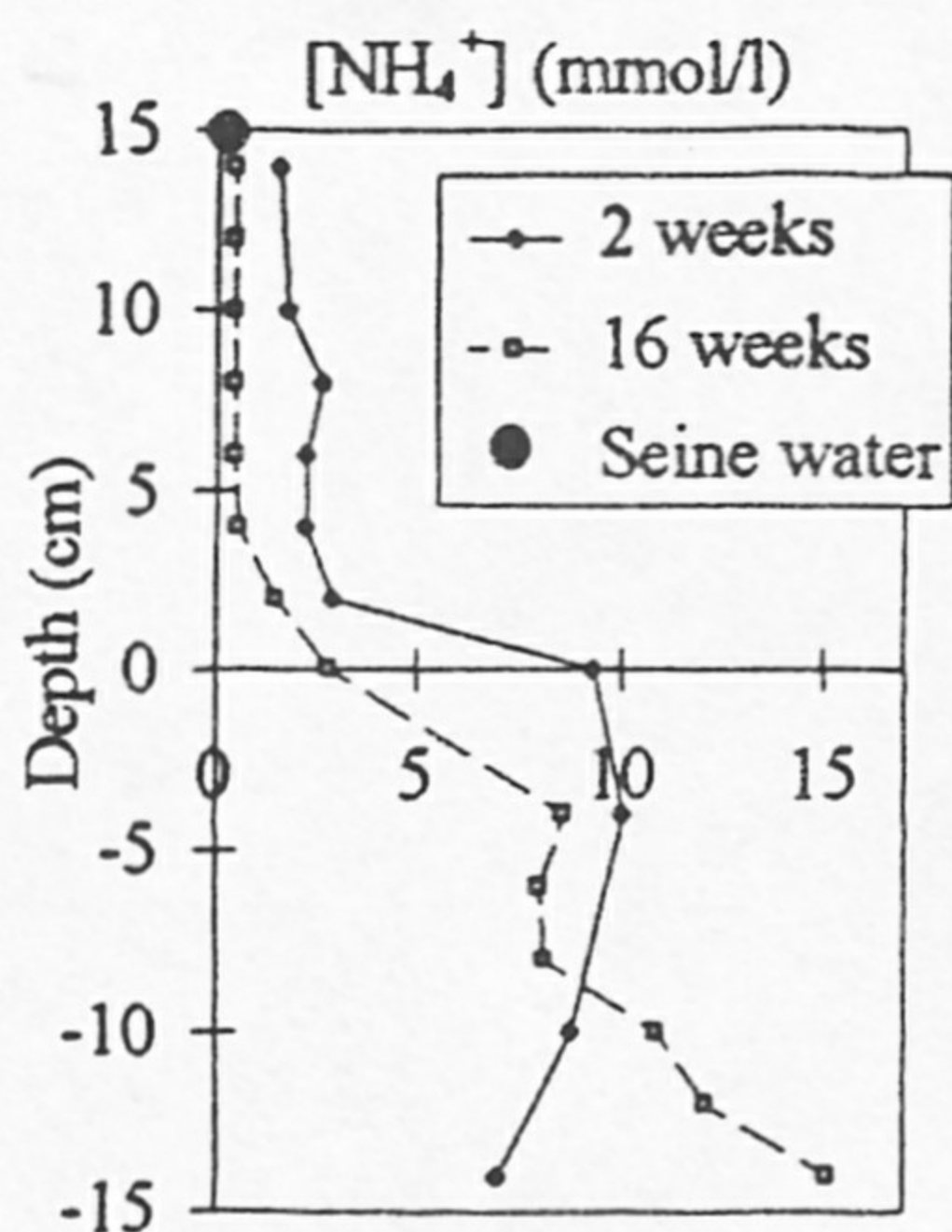


Figure 2: Dissolved ammonium profiles (2nd experiment)

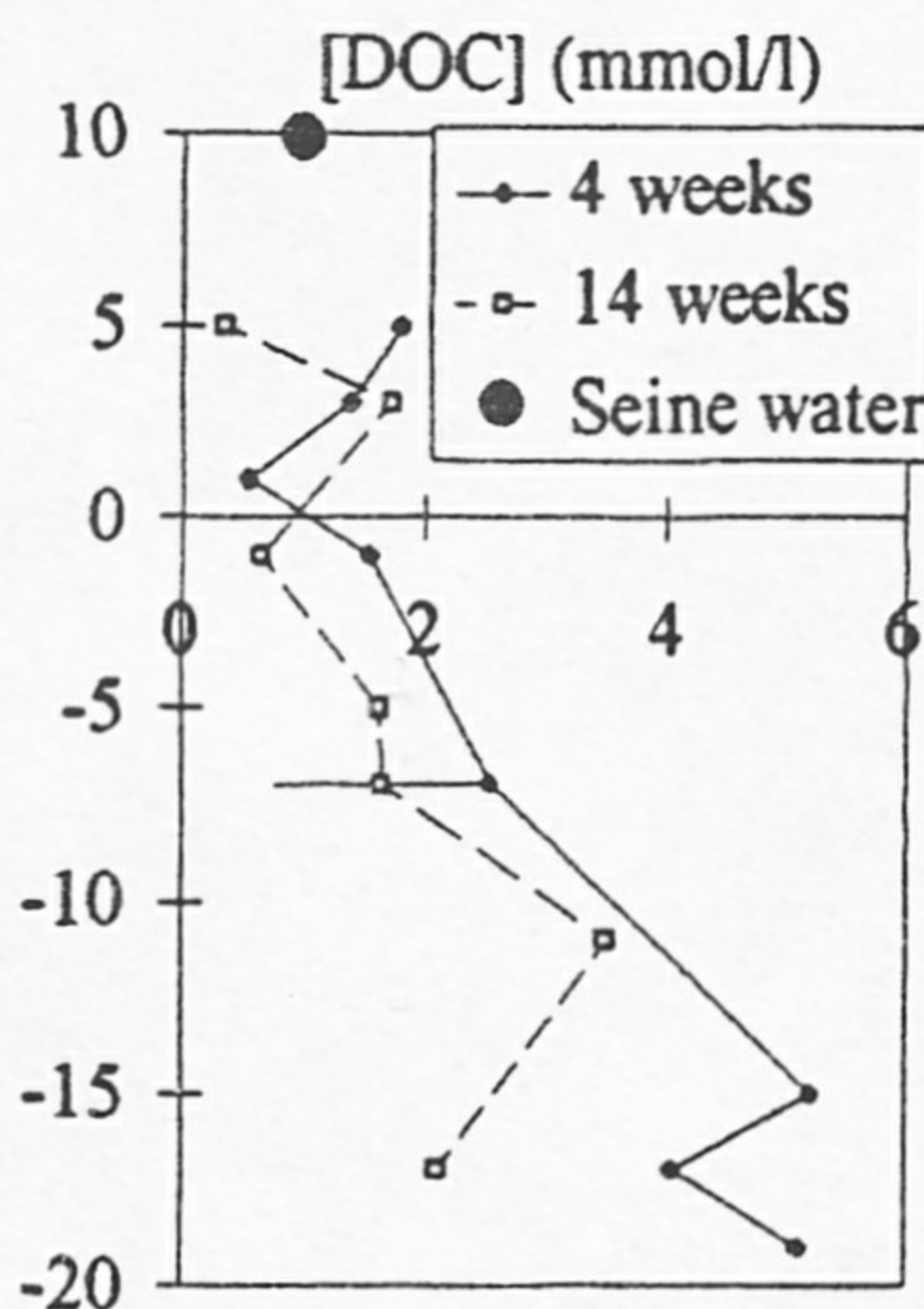


Figure 3: Dissolved organic carbon profiles (1st experiment)

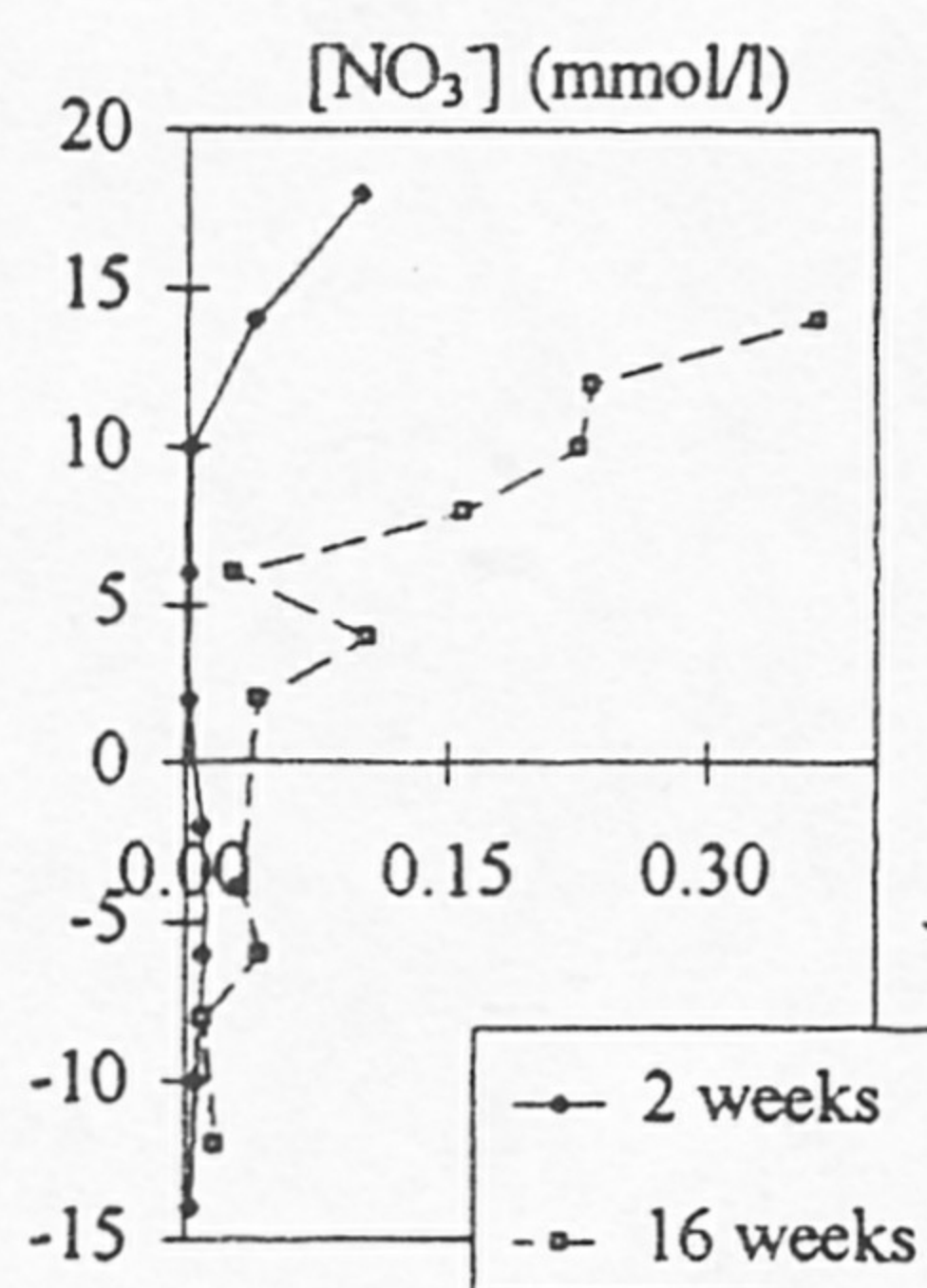


Figure 4: Dissolved nitrate profiles (2nd experiment)

Figure 2 shows ammonium results from the second experiment. The second and the last sample collections are presented, *i.e.* after 2 and 16 weeks of sediment evolution. Between these two interstitial water collections, the dissolved ammonium profiles do not show significant difference. Ammonium is one of the representative species produced during the degradation of organic matter. The water-sediment gradient settling rate and the high levels measured in the interstitial water demonstrate that a bacterial activity starts at the very beginning of the experience and continue during the study. An equilibrated profile is quickly obtained. This gradient indicates the occurrence of an ammonium flux from the bottom of the sediment column, where the activity is highest, to the top, where ammonium is oxidised by aerobic bacteria to nitrite and nitrate species (Berner, 1971).

Figure 3 shows an increase of the dissolved organic carbon (DOC) concentration in pore water with increasing sediment depth. As for ammonium ions, the DOC gradient demonstrates the degradation of particular organic matter and corroborates the strong bacterial activity mentioned above.

Figure 4 presents the dissolved nitrate profiles after 2 and 16 weeks of sediment evolution, during the second experiment. After two weeks of evolution, a large part of the nitrates present in the river Seine (initially measured at 0.4 mmol/l) is consumed. The last sample collection occurred 8 days after the addition of fresh Seine water, following an important loss of circulating water. Then, nitrates are still present at high levels in the overlying water. The last profile reveals a redox gradient in the overlying water about 5-10 cm above the water-sediment interface. Such water column heterogeneity, which was observed during the first experiment, is confirmed by the profiles obtained for sulphate and sulphide species during the same period. A large part of the oxygen carried by aerated circulating water is consumed at the water-sediment interface, and the redox potential decreases within the few centimetres of stationary overlying water.

Metal evolution

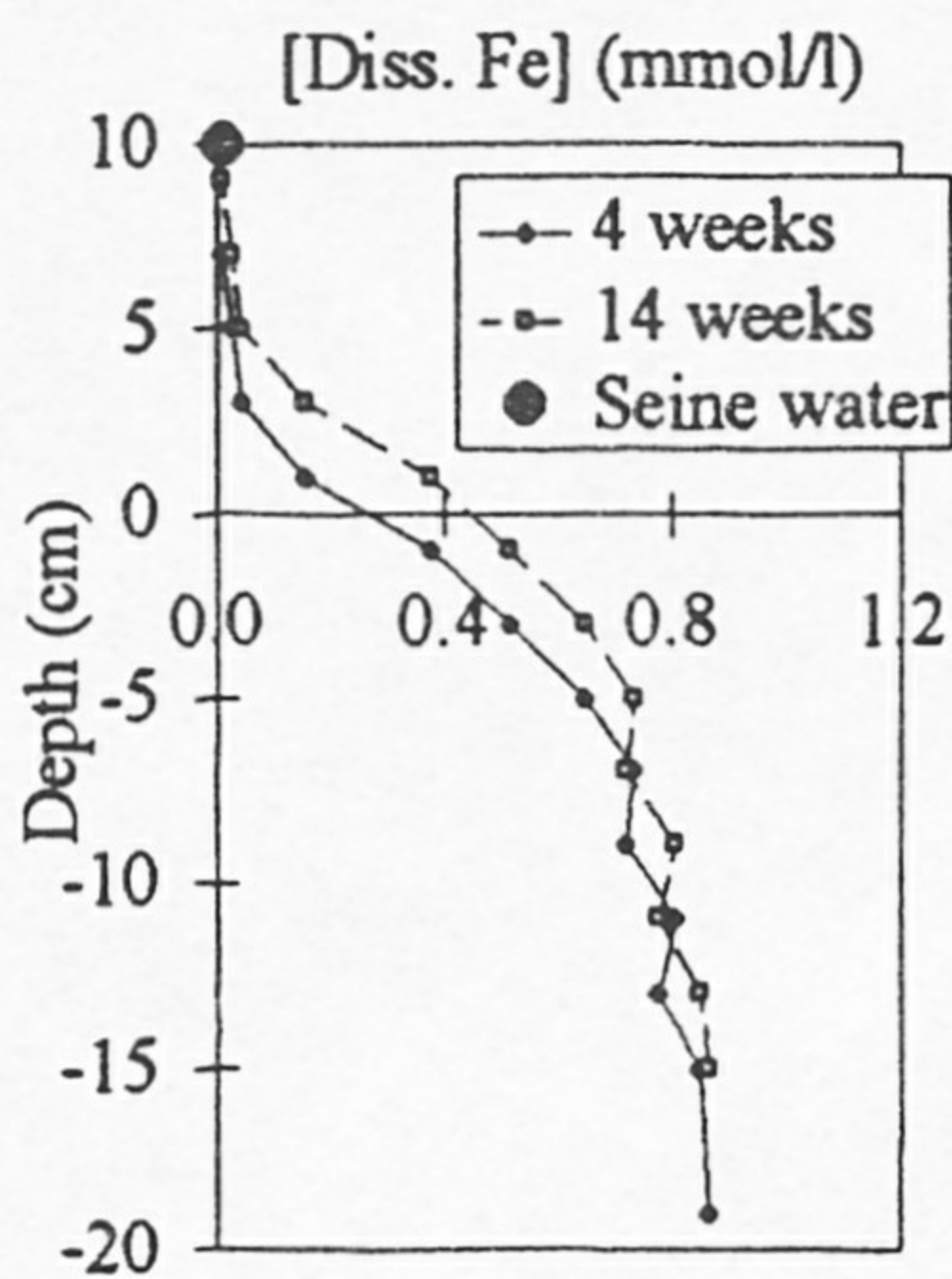


Figure 5 : Dissolved iron profiles (1st exp.)

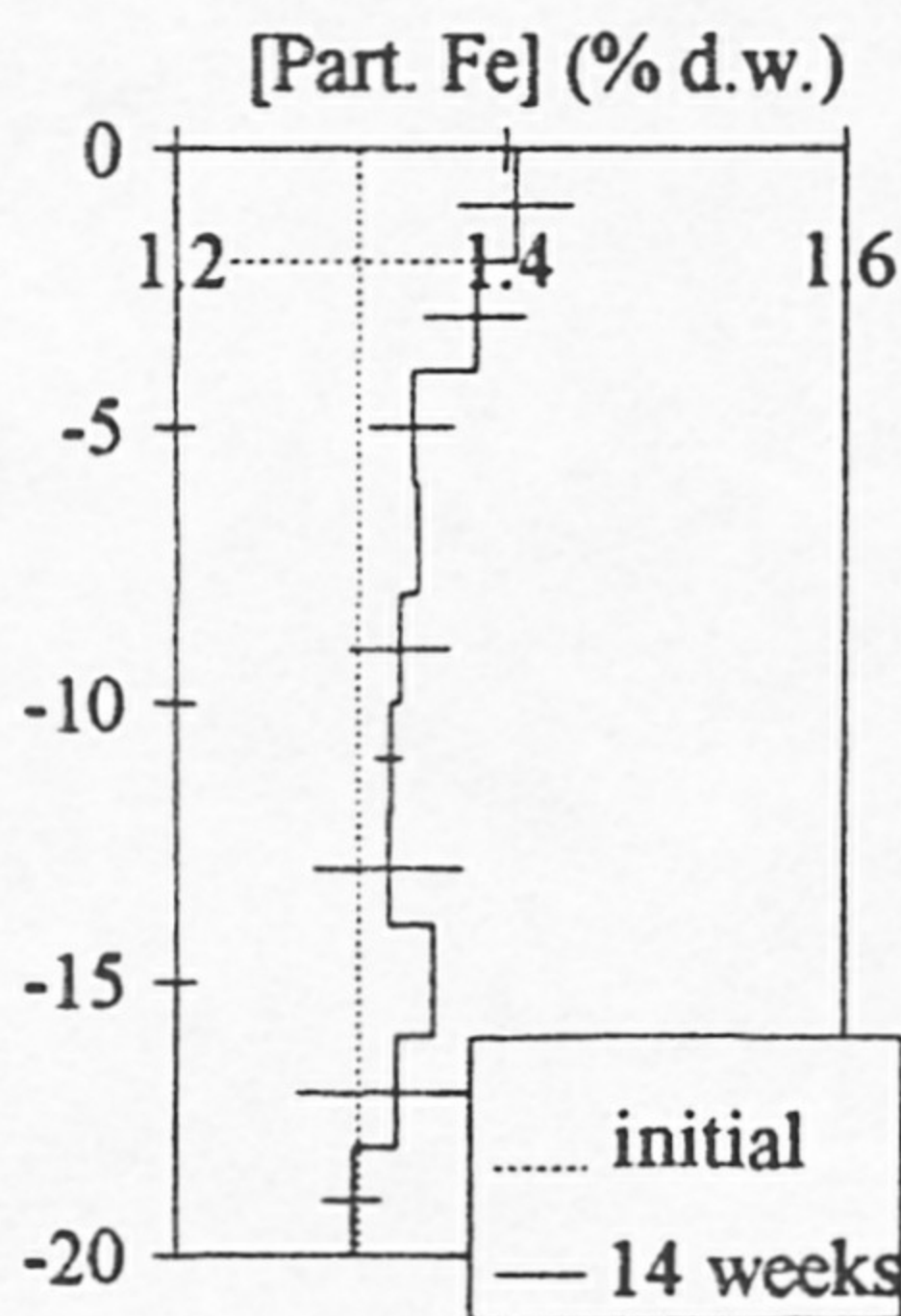


Figure 6 : Particulate iron profiles (1st exp.)

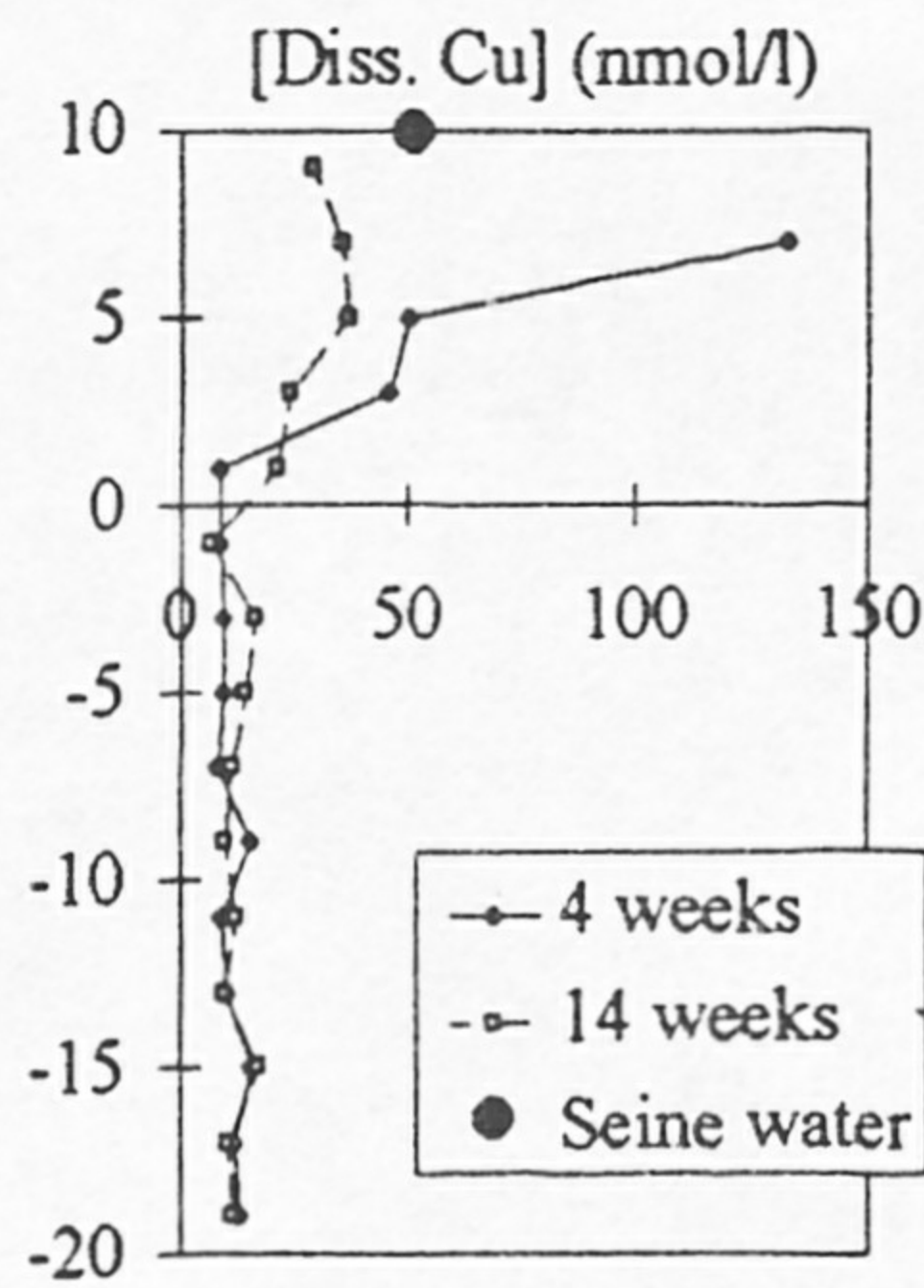


Figure 7: Dissolved copper profiles (1st exp.)

The dissolved iron profile is stable all along the period of the study (figure 5) and again

demonstrates sediment diagenesis processes. The intense biologic activity produces the redox potential decrease and the reduction of Fe (III), present under an insoluble hydroxide form $\text{Fe}(\text{OH})_3\downarrow$, into dissolved Fe^{2+} . A part of Fe^{2+} ions diffuses toward water-sediment interface where it is again oxidised, and thus precipitated. The figure 6 shows that, at the water-sediment interface, there is a new-born increase of particulate iron. The rest of dissolved Fe^{2+} is complexed by sulphur, and precipitates as amorphous iron sulphides $\text{FeS}\downarrow$. Calculation of the saturation index of $\text{FeS}\downarrow$ shows that this compound is able to precipitate through all the sediment column.

The copper profile presents a quite different pattern than iron (figure 7). The dissolved concentration is constant through out the whole sediment column (15 nmol/l). A higher level is measured at the top of the overlying water, which creates a gradient in the aqueous phase. The circulating-water copper concentration decreases also all along the study. Therefore, the sediment may be considered as a sink for dissolved copper. The saturation index for copper sulphides reveals that pore waters are highly over-saturated with regard to covellite $\text{CuS}\downarrow$. Another reaction may compete with the precipitation of $\text{CuS}\downarrow$: the complexation of copper with the dissolved organic carbon, released during particulate organic matter degradation.

Dissolved zinc and cadmium concentrations are constant through time and space. Their levels in interstitial waters are lower than 1 nmol/l. These concentrations imply that pore waters are under-saturated with regard to zinc and cadmium sulphides. Thus, other compounds may control dissolved concentrations in interstitial water for these heavy metals during sediment diagenesis.

CONCLUSION

In order to study the impact of CSO's on the river Seine ecosystem, field campaigns are necessary. However, a laboratory simulation overcome most of the difficulties that are associated to field studies. During this laboratory study, a high microbial activity has been observed in the sediment column, starting from the very beginning of the experiment. Organic matter degradation generates anoxic conditions, displayed by the very low levels of main oxidised species, like nitrates and sulphates. A large amount of ferrous iron produced in the sediment column is oxidised and precipitated at the water-sediment interface as ferric hydroxides. Moreover, the CSO contaminated sediments play a role of sink for heavy metal such as copper. Zinc and cadmium dissolved concentrations do not seem to be influenced by the presence of sulphides in pore waters.

Analysis in progress should enable the determination of kinetics for river sediment evolution and of dissolved metals fluxes towards the water-sediment interface. These laboratory results should then be compared to *in situ* observations, using peepers and sediment cores. An important finding, issued from these laboratory experiments, is that the establishment of quasi steady-state diagenetic profiles in interstitial waters is quite fast.

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